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Solidification Studies of some Copper - Based Alloys

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Stockholm

1973

SOLIDIFICATION STUDIES OF SOME COPPER-BASED ALLOYS

Lars-Martin Liljenvall

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AVHANDLING

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Solidification Studies of some Copper-Based Alloys

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This thesis reviews the development of micro- and macro-structure during solidification of metallic melts. The experimental work has been performed on copper-base alloys. A resumé of work presented in the following list is also given.

I. Bäckerud, L and Liljenvall, L-M
Study of solidification characteristics of some constitutionally different copper alloys.

Contribution to an International Conference on "Copper and Its Alloys" in Amsterdam 21-25 sept. 1970. Inst. of Metals 1970

II. Bäckerud, L and Liljenvall, L-M
Solidification characteristics of seven constitutionally different binary copper alloys. I. Crystal-growth conditions and morphology. J. Inst. Metals 100 (1973) 357-366

III. Bäckerud, L and Liljenvall, L-M
Solidification characteristics of seven constitutionally different binary copper alloys. II. The influence of crystal-growth conditions on structure development. J. Inst. Metals 100 (1973) 366-372

IV. Liljenvall, L-M
Solidification characteristics of twelve commercially different types of copper base alloys.

To be published

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ABSTRACT

The work deals with the development of the micro- and the macrostructures obtained under conditions, similar to those existing in ingots and castings.

The microstructure, obtained under different thermal conditions are outlined and special attention is given to the development of the microstructure in some copper-based alloys.

Different mechanisms for the development of macrostructure are described and the structure obtained by various nucleation processes during solidification of some copper-based alloys are discussed.

1. INTRODUCTION

An essential factor in production of castings and ingots is a good knowledge of the variables, which influence the development of the micro- as well as macrostructures, obtained during the solidification process.

The microstructure may be affected by several variables among which the most important are the composition of the material, the constitution of the alloying system and the cooling-rate. These factors influence to a great extent the developed structure and a good knowledge of the mechanisms is necessary in predicting the micro-structure of a desired material.

The macrostructure of a material can be developed by several mechanisms during solidification. A study of the developed structures in different materials and a correlation between these and the variables above mentioned may shed some light on the mechanisms prevailing during the solidification process.

The purpose of this work was to study the crystal morphology and to relate it to the different values of the growth undercooling developed at various compositions, constitutions and rates of heat transfer.

The work has also been devoted the study of the development of the various types of macrostructures, obtained under influence of different nucleation and growth mechanisms during the solidification process.

2. HISTORICAL BACKGROUND

Solidifying metals in a dendritic manner was described in a work by Tschernoff already in 1868. Ten years later he published, for that time, a very epochal work describing dendrite crystals in shrinkage cavities in steel ingots (5). The crystals seemed to have an octahedral configuration and an often published sketch of a dendrite from that work is shown in figure 1 . He furthermore observed that branches of second, third and higher orders could be noticed, developed from the main dendritic stalk.

Around one hundred years before Tschernoff´s work, Grignon (6) made a study of crystal morphology in shrinkage cavities in cast iron. He noticed that the dendrites, developed during a very slow solidification process were multiple-branched.

However, already in 1540, Biringuccio (7) reported that segregations had been observed in studied materials. He also reported that a fractured surface showed a granular appearance.

It is surely true that already the ancient metallurgists understood the essential relation between short range segregation (microsegregation) and long range order (macrosegregation).

In the late 1700-th century, Boyle (8) recognized that crystal morphology could be arranged in two ways: a random arrangement or aligned in a directional manner. In 1724 de Réaumur (9) made a study in metals and showed that they consisted of crystals of various sizes.

During that century between the work of Grignon and Tschernoff there were many published papers by various investigators dealing with different subjects in the field of crystal growth (6).

Mechanical vibration of the melt during the solidification is sometimes used to produce grain refinement. It is interesting to note that this, already in 1829,

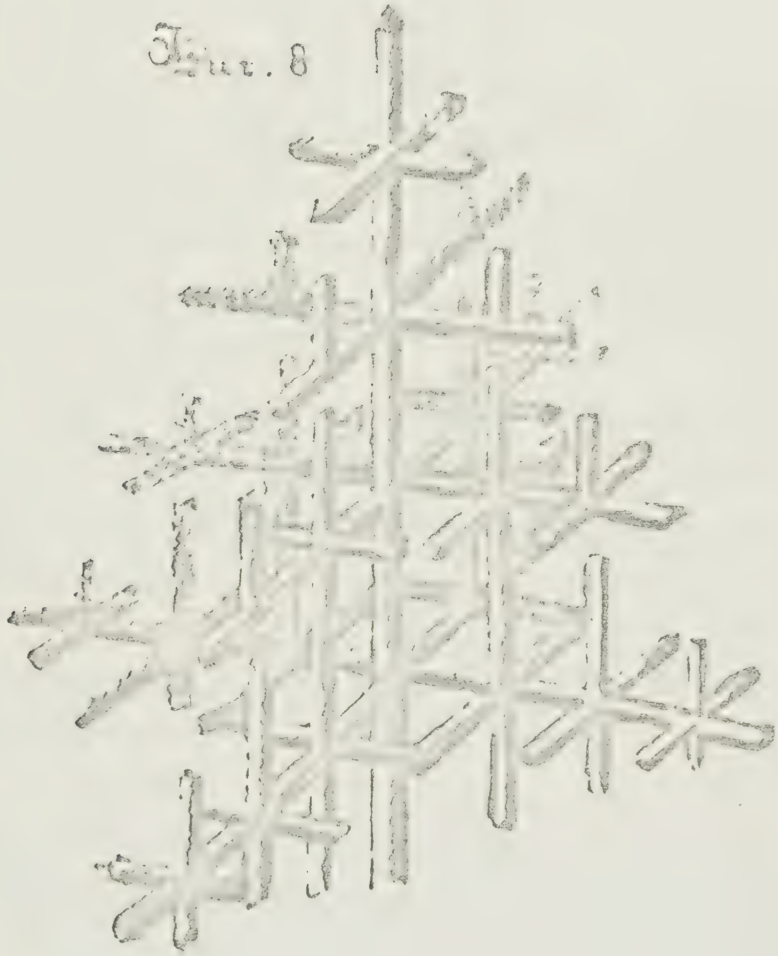


Figure 1 Sketch of a dendrite. After (5).

has been tried by Savart (10). He found that the crystal system was disturbed during the vibration and he also studied the mechanical properties in the metal after this treatment.

Though many works concerning structure and crystal morphology have been published during the 18 th- and 19 th centuries, this had very little importance on the development of better casting techniques and casting processes. In 1903, however, a german chemist, Gustav Tammann, began to publish comprehensive series of constitutional diagrams. This work and many other from him and his collaborators dominate a new period of metallurgical research. In the field of solidification he introduced observation of organic substances and studied several relationships between crystal structure and undercooling.

In the early 1910's the general accepted theory was that solidification could be divided in nucleation and growth. It was also pointed out that the interior of an ingot consists of crystals which have grown from centers independent of the outer rim of crystals.

Two of the works published during the 1920's by Genders (11) and Desch (12) are of special interest and shortly outlined here.

Genders (11) postulates that there must be an undercooling at the solid/liquid interface at any solidification process. He also says that columnar growth will occur if the material of the center of a casting remains liquid, but should the casting temperature be low, crystallization may occur at any isolated centers in the interior and then grow to equiaxed crystals.

He also emphazised the effect of the freezing range on the equiaxed zone. He postulated that it is the longfreezing range alloys that show equiaxed crystals - he explained this in terms of a layer adjacent to the interface in which the concentration is low in terms of the high melting-points material. Ahead of this layer, liquid of higher solute composition exists, which can be low enough in temperature to be in the range for independent crystallization.

Genders also states when the metal has virtually none, or only a small freezing range, the surface of solidification should be smooth, and with a positive temperature gradient no independent centers of crystallization should develop because no part of the liquid is undercooled. As he pointed out, to have a large undercooling ahead of such an interface, an inverse temperature gradient in the liquid is necessary, a condition which would not occur in the centre of castings.

Genders also explains the presence of some equiaxed crystals in terms of inoculation of the metastable undercooled liquid. He thought that the nuclei are formed during cooling in the chill zone of the ingot and transported by the turbulent liquid into the interior of the melt. This suggestion is very similar to one made by Chalmers (13) many years later.

In the other work published during the 1920´s, Desch (12) also describes the columnar zone of the ingots as follows: " The change from the confused outer layer of minute crystals to the columnar zone is regarded as due to natural selection. The original nuclei may have any orientation, but only those which have a direction of rapid growth perpendicular, or nearly so, to the wall survive".

Furthermore, when discussing the equiaxed zone, Desch thought that the crystals in this zone were formed under homogeneous nucleation conditions: "When the temperature has fallen so far it is possible for a crystal to exist, a few colliding molecules may fail to rebound, and so become attached to one another, the balance being the attracting and repelling forces between them causing them to arrange themselves on a space lattic".

Even more investigators have by degree published works within this field which more and more have made clear the mechanisms associated with the field of solidification. Hultgren (14), who began his works in the 1920´s, shows that the columnar crystals in an ingot could be varied by changes in, for example, the casting temperature and the stirring during the solidification.

During the 1930's, the works by Northcott have to be mentioned. 1938 he explained (15) the influence of varying additions to copper. He found that during growth elements adsorb to some extent at the solid/liquid interface and slowed down the rate of growth. From our point of view, Northcott discussed the phenomenon of constitutional supercooling - a theory which in the beginning of 1950's was proposed by Rutter and Chalmers (16).

Futhermore, in a paper from 1934, Northcott (17) antecipates the theory that columnar growth ceased when the ingot had contracted so much during solidification that it separated from the mould.

As in any field of science during the late decades in this century, solidification and crystal growth have developed to a great extent. This can be measured by the increasing amount of articles published in the subject.

A critical summary of the most important work within this area which have been published up to 1950 have been published by Chalmers (18).

DEVELOPMENT OF MICROSTRUCTURE

1 General

The structure of a solidified material can consist of heterogenities as undesirable segregation pattern (distribution of the alloying element in the material), pores, pipes and various other faults developed during the solidification process and which can cause the material to be unusuable industrially.

To get rid of, for example, the undesirable segregation pattern in ingots and castings, homogenisation treatment of the material is often accomplished. However, if the material has such a structure and size that homogenization treatment does not change the structure in the whole material to a desirable amount within a practical lapse of time, it would not be economically excusable to heat treat them. It is therefore necessary to know the theory behind the solidification process to get a satisfactory quality of finished material and thus be able to control the structure of the solidification process.

The structure, developed during solidification, depends on a multitude of factors, among which the most important are:

- the composition of the melt
- the constitution of the alloy system
- the thermal factors at the solidification process (i.e. temperature and rate and direction of heat transfer)
- mass transport (convection in the melt and diffusion phenomena in the melt and in the solid)
- surface energy phenomena
- kinetics of interface reactions

2 The developed structure

During the solidification of nearly all alloy systems, which have been produced by normal casting processes, plane front solidification occurs. Such a steep

temperature gradient, which is necessary for growth of a plane front does not develop during the thermal conditions available at the solidification of commercial materials.

The microstructures, which develop, favoured by the actual thermal gradient at practical applicable solidification conditions, mainly consist of cells, dendrites or sometimes a type of transition morphology called cellular-dendritic structure.

3 Development of microstructure under different thermal conditions

3.1 General

The thermal gradient, $\frac{dT}{dx}$, which develops in the melt during solidification, can be obviously negative, obviously positive or close to zero and in these special cases give rise to different structures of the growing solid phase. The principle features of each case are briefly outlined below.

3.2 Obviously negative temperature gradient in the melt

When considering the growth of a pure melt or an alloy in a negative temperature gradient, the liquid ahead of the interface is thermally undercooled. When an outgrowth is formed on the interface, the tip of this projects into a region of greater undercooling, which is a factor which tends to accelerate the growth of this protrusion. The latent heat, evolved during growth is, however, a growth-preventing factor because of its tendency of lowering the degree of undercooling in front of the interface. An equilibrium is thus established between emitted latent heat and supplied material at a special degree of undercooling.

With this equilibrium is joined a certain morphology, which depends on the prevailing emission of latent heat. If the undercooling of the melt is changed for some reasons, the above equilibrium condition is also changed in such a way that a new one is established between evolved latent heat and supplied material at this new situation. The morphology of the crystal is thereby changed.

For example, if the undercooling of the melt is increased, this effect a greater driving force for the growth of the crystals. As a result, these crystals may emit more latent heat/time and this may occur if the surface of the crystals is increased, i.e. if more branches are developed.

Thus, growth of the crystals in an undercooled melt occurs preferably dendritically, a case, which has been theoretically studied by Horway and Cahn (19).

Tiller (20) has also devoted this case a detailed study. Figure 2 illustrates that condition when the latent heat, evolved from the growing solid, is transported from the solid phase and out into the surrounding melt and the principle temperatures involved during this process are also given.

T_e is the equilibrium melting point of the solid. The temperature difference ($T_e - T_{e_1}$), which often is designated ΔT_S, is the depression in temperature caused by the solute build-up ahead of the growing solid phase. The temperature difference ($T_{e_1} - T_{e_2}$) (= ΔT_R), is the change in temperature due to the curvature of the surface of the growing crystal. T_i is the temperature of the interface and T_∞ is the temperature of the surrounding undercooled melt. The temperature difference ($T_{e_2} - T_i$) (= ΔT_K) is controlling the rate of atomic deposition from the melt on the solid depending upon the particular operative attachement mechanism. Finally, the temperature difference ($T_i - T_\infty$) is used for the dissipation of the evolved latent heat to the surroundings and thus controls the macroscopic freezing rate at a specific point on the surface. The sum of these temperature depressions is called ΔT_{tot} and is the undercooling which gives the driving force for the growth of the particle.

3.3 Obviously positive temperature gradient in the melt

When considering a growth of a pure metal in a positive temperature gradient and in contact with a cold environment, two special cases may be observed.

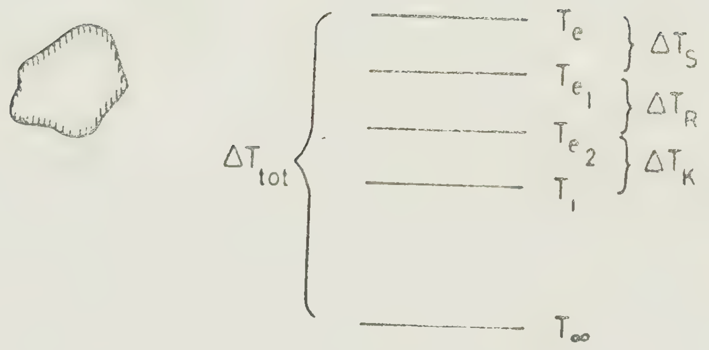


Figure 2 Particle of a solid in an undercooled melt and important temperatures involved in the formation of solid at any point on the surface. After (20).

2.2.2.1 Constant positive thermal gradient in the melt

The temperature gradient is kept constant in the melt during the whole process and this can be maintained by supplying heat to the melt and remove it through the solid.

If a pure melt is considered the advancing interface is planar and coincide with that temperature at which solidification occurs, i.e. at a temperature just below the equilibrium temperature. That means that practically all of the melt in front of the growing interface is above its melting-point.

If a protrusion on the interface grows away into the melt, it reaches a region, which has a higher temperature. This means that the growth of the protrusion ceases and the planar interface is reestablished.

If an alloy is considered the situation may be illustrated by figure 3 . If an alloy system with a distribution coefficient less than unity is considered, the advancing solid front accumulates the solute in front of the interface and thus a concentration profile is developed in the melt. From this profile it is possible to plot the equilibrium temperature redistribution in the liquid in front of the interface.

The transformation from a plane front solidification to the development of cellular sub-structure, observed by Rutter and Chalmers (16) when studying the solidification interface morphology, develops as a consequence of the formation of a constitutionally supercooled zone in the melt adjacent to the interface.

The existence of this zone ahead of a planar interface is given by the following conditions:

$$\frac{G}{R} < \frac{-m\,C_S\,(1-k_0)}{k_0\,D_L}$$

where

G is the temperature gradient in the liquid at the interface

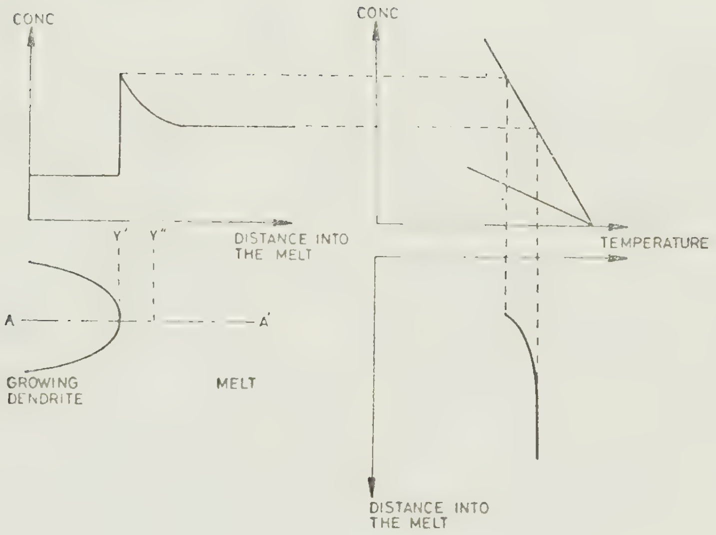


Figure 3 The solute and the liquidus temperature redistribution in front of a growing dendrite tip.

m is the liquidus slope

C_S is the concentration in the solid at the interface

R is the cooling rate

D is the diffusion constant of the solute element in the liquid phase

k is the distribution coefficient.

From this it is obvious that the morphology of the solid phase, besides the temperature gradient, is depending on R, C_S, k, D_L, and m, defined above.

This equation was first derived by Tiller et al (21).

Superimposed on the figure 4, showing the liquidus equilibrium temperature distribution, T_E, three actual temperature distributions, T_A, are plotted. If the slope of the T_A-lines are so steep that there are no intersections with the curve for the equilibrium liquidus temperature, T_E, plane front solidification is maintained. On the other hand, if the actual temperature partly lies under the T_E-curve, a zone of constitutional undercooling is developed, which is responsible for instability at the interface. Figure 5, taken from Tiller (20), shows the effect of various degrees of constitutional supercoolings on interface morphologies in this transition regions.

It can be seen that with decreasing value of the thermal gradient, the structure will transform from a planar interface (developed at a very steep temperature gradient) via a pox-like structure and various types of irregular cell-formations to cells with hexagonal cross-sections.

.3.1.1 Effect of cooling rate

Under the assumption that the composition and the alloying system are maintained, the solidified crystal morphology can be changed by varying the temperature gradient in the solid/liquid region, by changing the rate of heat transfer. If the cooling-rate is increased, the linear solidification interval b (see figure 6 a) at the solidifying front diminish and the solid phase get a more cellular structure which is elucidated in figure 6 b. On other hand, if the cooling rate is diminished the linear solidification interval elongates, figure

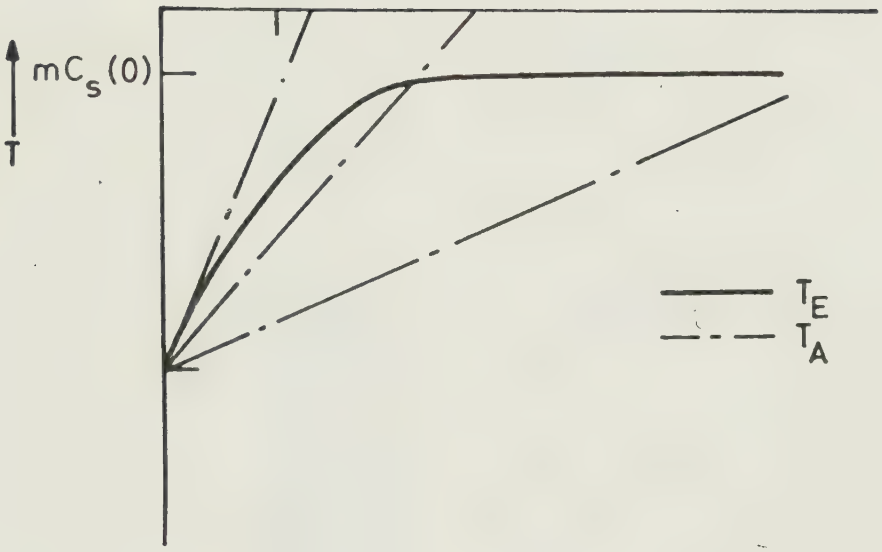


Figure 4 Illustration of the development of the zone of constitutional supercooling in the liquid at three different actual thermal gradients, T_A. T_E is the equilibrium liquidus temperature distribution.

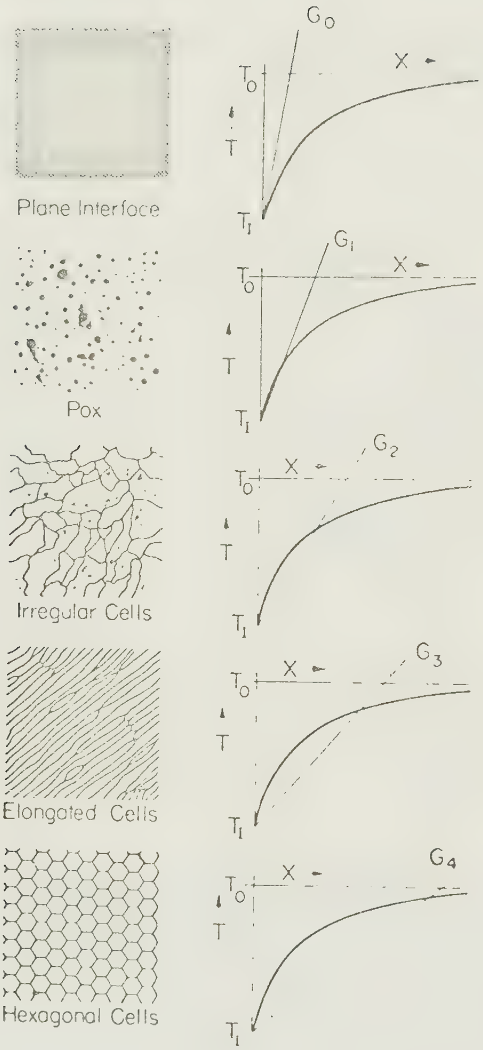
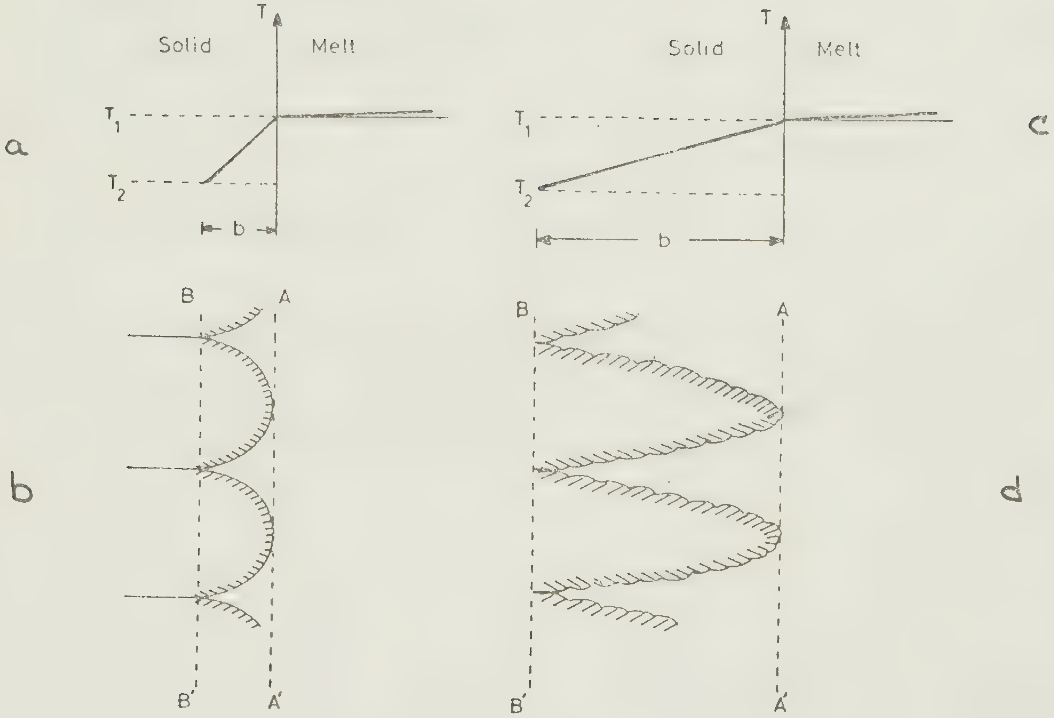


Figure 5 Various morphologies obtained at different values of the constitutional supercooling. After (20).



Figures 6 a – d Crystal morphologies obtained at different cooling rates represented by different thermal gradients in the solid.

T_1 and T_2 represent the temperatures for the beginning and the end of solidification.

The "linear solidification interval" is designated "b".

Fig 6b shows a cellular structure, obtained at a relatively steep temperature gradient, shown in Figure 6a. Figure 6d shows a cellular-dendritic structure, obtained at a less steeper temperature gradient, shown in 6c.

6 c, and the caps of the cells reach such a position in their growth that they project far into the melt. The development of pretubations is favourable in the lateral direction around the cells. This situation produce the start point for side-branching of the cells and is here called the cellular to dendritic transformation, figure 6 d. This has been experimentally found to depend of the value of $\frac{C}{V^{1/2}}$, found by Tiller and Rutter. Data for the cellular and the dendrite transformation conditions are given in figure 7, (22).

3.3.1.2 Effect of freezing-range

In alloy systems with similar constitution but different freezing ranges various crystal morphologies may develop. The larger freezing range the more branching crystals are to be expected. See figure 8 a-d.

3.3.1.3 Effect of composition

In a given alloy system and under given freezing conditions, the solidified structure may pass various morphologies with increasing concentration. Side-branches, due to lateral instabilities, may develop and a dendritic structure is obtained.

As can be concluded from the above discussion, there is possibilities for development of vastly different structures from plane front, via cells and cellular-dendrites to dendrites with increasing concentration of the alloying element. In spite of that the growth occurs in a positive temperature gradient this structure development is due to the effect of the constitutional undercooling.

3.3.2 Variable positive thermal gradient in the melt

A variable temperature gradient is often found in the beginning of a freezing process when crystals formed at a cold mould wall grow inwards into a supercooled melt.

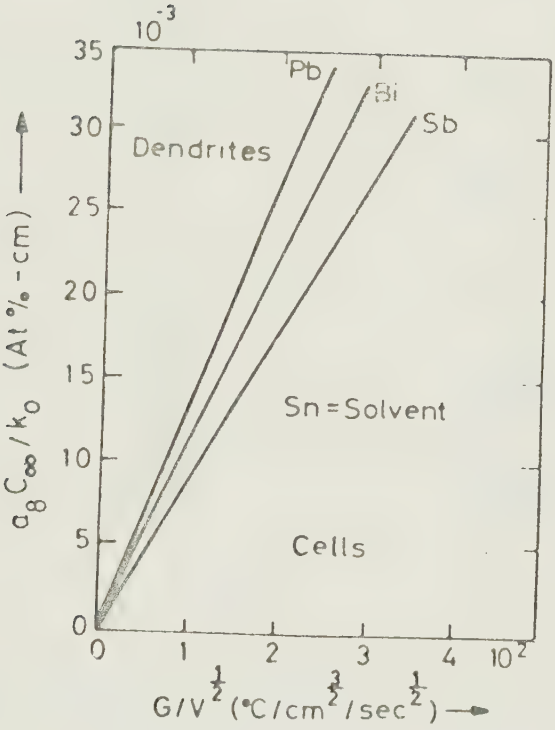


Figure 7 Plot of $a_6 C_o/k_o$ versus $G/V^{\frac{1}{2}}$ for the cell interface- dendritic interface transition in Sn. After (22).

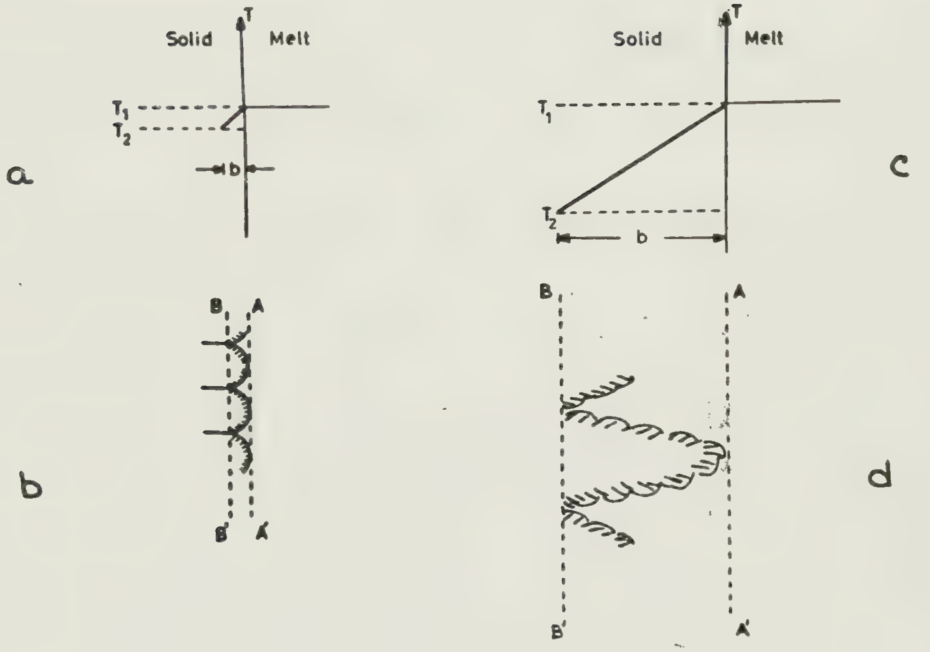


Figure 8 The temperature gradients, Figure 8a and 8c, and the linear solidification intervals, "b", at two different freezing ranges considered at the same rate of heat transfer. The principle sketches of the belonging morphologies are also given, Figure 8b and 8d.

In normal casting processes this superheat is however gradually lost. The first part of the columnar type of crystals therefore grow in a continously changing temperature gradient.

3.3.4 Negligible temperature gradient in the melt

As mentioned in the preceding chapter, the beginning of the growth occur in a continously decreasing temperature gradient.

When the overtemperature of the melt has decreased to that extent that a smooth temperature distribution is obtained in the melt, the growth of the columnar crystals continue into a liquid of zero (or at least a very small) temperature gradient and the rate of growth is only controlled by the extraction of the latent heat of fusion through the already solidified material and the mould wall and not restricted by the supply of heat from the interior of the melt. By changing the amount of this heat transport (i.e. by varying the external temperature by different ways of cooling), the crystal morphology can be influenced, in principle in the same directions as described above for crystal growth in a positive temperature gradient (section 3.3.3.1)..

4 Studies of the development of microstructure in some copper-based alloys

4.1 General

In the foregoing section structure development during solidification under different conditions has been discussed.

The structure development in one of these cases, i.e. at a near zero temperature gradient in the melt, has been investigated by Bäckerud and Chalmers (23), in the solidification study of aluminium alloys. They correlated the solidified structure with the measurements of the growth temperature of the dendrite tips, which is mainly influenced by the rate of heat transfer, composition and the constitution of the alloy.

It has to be mentioned that this investigation was one of the first in which the assumption was made that a zero (or near zero) temperature gradient is at hand in a solidifying melt and the experiments showed that this was the case.

To continue in working with these results and experiences and to apply them to another base material, experiments have been performed on copper-base materials. In a work by Bäckerud and Liljenvall (2), seven various binary copper-base alloys have been chosen to represent constitutionally different types of these alloys. The effect of composition, constitution and cooling rates on the growth temperature and on the morphology have been studied and the results of this investigation is out-lined below.

4.2 The growth induced undercooling

A general cooling curve from the solidification of a binary alloy is shown in figure 1 in (2). After undercooling before nucleation and after the recalescense the temperature remains nearly constant. This temperature recorded must be very close to that of the tips of the growing crystals, as the temperature gradient in the melt is close to zero.

If the cooling rate is changed, the type of steady state conditions obtained at a special rate of heat transfer is also changed. This means that the growth undercooling also changes as does the morphology of the crystals.

The general appearance of the actual growth temperature as function of the cooling-rate is shown in figure 4 in (2) as measured in a copper- 5 % silver alloy.

The composition of the alloy is another variable among the important ones, which influences the temperature of growth. Is an increasing amount of alloying element added to a pure metal, the growth undercooling is increased to a maximum level called the value of saturation, which is characteristic for the alloy system. Figure 5 in (2) show this relationship.

With this change in the temperature of growth is connected a change in the crystal morphology, from cells to dendrites. It has been shown in this investigation of copper-base alloys that this change in morphology is completed when a "saturation value" in ΔT is reached. It is therefore concluded that there is a relationship between the undercooling for growth and the developed morphology. In the work by Bäckerud and Liljenvall (2), all the ΔT/%-curves for the investigated alloys have been collected in figure 19 in (2). The effect of the various alloys i.e. various constitutions on the undercooling at a given rate of heat transfer is shown. To each of these curves also belongs a d_{min}/%-curve (not shown in this figure but in the special figures shown for each [illegible]). [illegible] distribution coefficient, as in the copper-bismuth system, shows a great value of the growth induced undercooling and this already at a small alloying concentration, on the contrary, for an alloy with a relatively high distribution coefficient, i.e. close to unity, as in copper-manganese system, there is a growth temperature, which only slightly differ from growth under equilibrium conditions. In the copper-bismuth case, the development of dendrites occurs already at a low concentration (the value of saturation occurs at a little concentration). For the copper-manganese case, this saturation occurs at a relatively high concentration of the alloying element and the solidified structure do not show any development of dendrites until this value.

4.3 The segregation distance

One usual way to present a numerical value to the morphology is to make a linear analysis of the dendrite arm spacing. This is a method which has been used by several investigators. In the actual work, however, also the cell width has been measured and thus another definition has to be stated. In one of the works (2) the minimum segregation distance, d_{min}, is presented, defined as the smallest periodically repeated distance between areas enriched (or impoverished) of alloying element. With this definition at hand it has been convenient to compare the various structures developed at different solidification characteristics, from cells via cellular-dendrites to the dendritic structure.

The figure 7 in (2) summarizes the effect of cooling rate on the minimum segregation distance, d_{min}, at various additions of alloying element. It is made clear from this figure that the variation in the segregation distance with the cooling rate diminish with increasing concentration of the alloying element. It is also noticed that the greatest change in crystal morphology is obtained at small alloying additions to the pure material.

From figure 18 in (2) the variaton of the segregation distance with the composition is presented for the whole materials in this investigation. It is clear that there is a marked change in morphology with increasing concentration for all systems investigated. It is also noticed, when reaching the value of saturation in the undercooling for growth there is only a slight difference in the morphologies with concentration and this has been observed for all the three cooling rates.

In a work by Liljenvall (4) concerning solidification behaviour in some commercial copper-based alloys, a difference of the segregation distance in the solidified structure has been observed at varying cooling rates. This change is not comparable with that great one observed at the initial addition of alloying element to a pure metal, but more comparable with the change in the dendritic structure observed after that the value of saturation has been reached at higher compositions.

This observed microstructure within the grains is of great engineering importance and have influence on properties of materials. For example, mechanical properties and corrosion resistance of cast metals are greatly influenced by the microsegregation and it has therefore been considerably interest in determining effects of solidification variables and establishing the mechanism of formation of the microstructure as cells and dendrites. It is therefore important to observe that the degree of homogenity which can be obtained in cast alloys by subsequent homogenization treatments is greatly influenced by the dendrite arm spacing and the mechanical properties of the heat-treated material depend on the homogenity obtained.

Among the physical conditions that could be expected to have an influence on the dendrite arm spacing that appears in cast metals and alloys are the composition, the type of constitution (differences in solid and liquid solubility, eutectics etc.), rate of freezing and the crystal structure.

.4.4 Experiments

Figure 9 shows some experimental data concerning the dendrite arm spacing studied in aluminium-4.5 % copper alloys. The data are compiled by Brody et al (24) from work of Brown and Adams (25), Michael and Bever (26), Reed (27), and Horwath and Mondolfo (28).

Generally, dendrite arm spacing is formed to be inversely proportional to the cooling rate (or directly proportional to the local solidification time).

In a work by Horwath and Mondolfo (28), who studied the variaton in dendrite spacing due to the cooling rate, the obtained results were in agreement with earlier published work by i.e. Spear and Gardner (29) and Brown and Adams (30).

The data from the investigation by Horwath and Mondolfo (28) has been plotted in figure 10 , where the dendrite arm spacing is measured as function of cooling rate, in degK/min, at different concentrations of copper in aluminium. The investigators pointed out that their results were in a good agreement with the data and results from an investigation by Michael and Bever (26) concerning aluminium containing 2, 3, 4, and 5 % copper. They concluded that the dendrite arm spacing increases with decreasing rate of solidification. This result in turn agrees with the result by Alexander and Rhines (31) who made their investigation on aluminium alloys containing 5, 10, and 20 per cent of copper as alloying element.

In an investigation made by Liljenvall (4), the dendrite arm spacing have been measured at three different cooling rates in some commercially important copper-base materials.

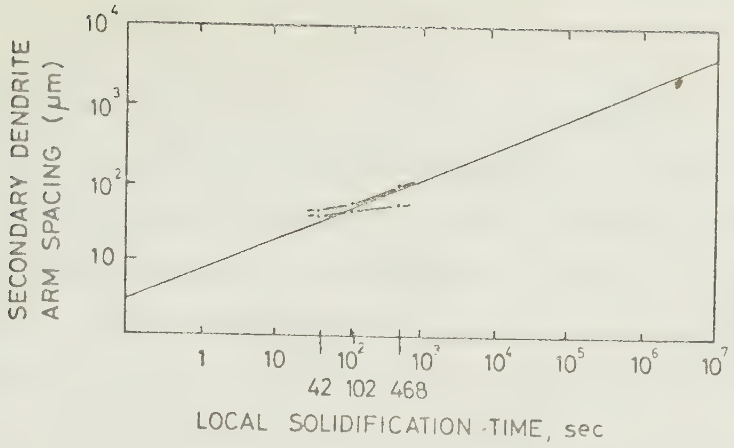


Figure 9 Dendrite arm spacing versus local solidific tion time for Al-4.5% Cu - alloy. After (24).

In the Figure is alos plotted two curves from the investiga- tion by Liljenvall (4) concerning commercial copper-base alloys.

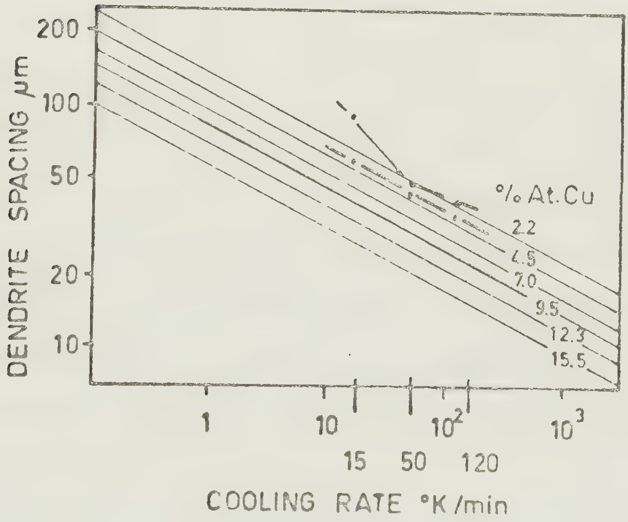


Figure 10 Dendrite arm spacing as function of cooling rate. After ([illegible]).

In the Figure is also plotted two curves from the investiga- tion by Liljenvall (4) concerning commercial copper-base alloys.

These curves show among themselves an appearance of similar character and can be presented as a well collected bundle of curves. The outhermost curves in this bundle have been plotted in figures 9 and 10 to be compared with the results obtained by earlier investigators. As can be seen from this comparison, the data obtained from the dendrite arm spacing in the copper-base alloys are in good agreement with the earlier published data though these were taken from aluminium base materials.

Refering to the work by Horwath and Mondolfo (28) and to the other earlier mentioned works concerning the dendrite spacing, it may be concluded that the dendrite spacing and its function of the cooling rate may own general applicability for other metallic materials.

Figure 3 in the work of Bäckerud and Liljenvall (2) shows in principle the influence of the composition on the values of minimum segregation of a copper-base alloy with the rate of heat transfer as the parameter. Typical crystal morphologies, showing this change in microsegregation is elucidated by the photo-micrographs of the copper-silver system in the same reference (2).

This change is furthermore in agreement with the observations made by Horwath and Mondolfo (28), who worked with the aluminium-copper system and there observed a decrease in dendrite spacing with increasing alloying concentration, see figure 11. Here also various cooling rates are plotted as the parameter. The increasing effect in dendrite spacing which is evident from the figure and obtained at concentrations higher than around 16.5 atomic-% copper is supposed to be influenced by the eutectic reaction.

However, Alexander and Rhines (31) have stated that " the dendrite arm spacing always increases with increasing concentration of the solute elements". This is in a direct contrast with the statesments of Horwath and Mondolfo (28) and the observations made by Bäckerud and Liljenvall (21).

Horwath and Mondolfo (28) have presented an explanation for this contradiction. Alexander and Rhines (31) measured the dendrite spacing on the ingot-disc, and only the dendrites, which had their primary stalks in the plane of the disc

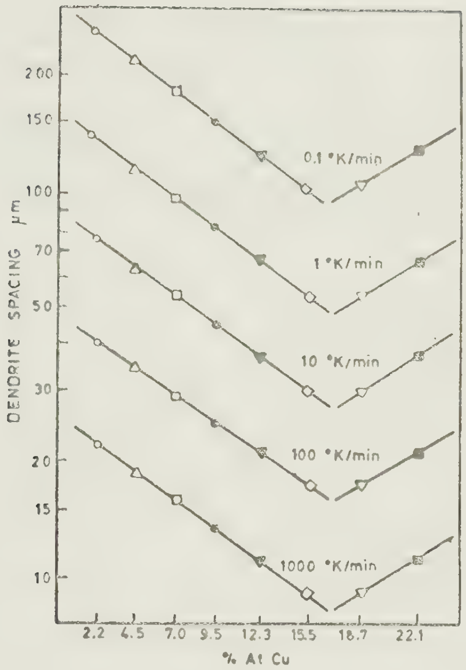


Figure 11 Dendrite spacing as function of copper content at different cooling rates. After (2[illegible]).

and were fully developed were considered. Unfortunately, this method to measure the secondary dendrite arm is not relevant because the mechanism for developing the secondary arms is thus ignored.

1.5 Grain size and dendrite spacing

Already Alexander and Rhines (31) stated that there is no apparent relationship between the grain size and the dendritic spacing in a casting, i.e., the dendritic spacing can vary significantly within a single grain. The increase in the columnar grain length, as the casting temperature is raised is not associated with a corresponding increase in dendrite spacing.

1. DEVELOPMENT OF MACROSTRUCTURE

1.1 General

The thermal conditions, determined by factors like heat extraction, rate through the mould walls and pouring temperature are of importance during solidification when building up the as-cast structure.

The final grain morphology of a solidified ingot or casting, can generally be described in terms of zones. Three different regions are frequently apparent in the macroscale in an etched ingot section: an outer "chill zone", a columnar zone, and a central, equiaxed zone.

The "chill zone" usually consists of equiaxed grains, which nucleate at or near the mould wall. The columnar zone has its long grains mainly orientated parallel to the direction of the heat transfer. The zone is a result of growth of favourable orientated grains, developed in the "chill zone". The long grain boundaries are often centres of weakness in the material where cracs often can appear during subsequent deformation. Finally, the equiaxed zone in the middle of the ingot, consist of coarse, equiaxed crystals. An ingot, consisting of all these zones is seen in figure 12 (32).

An ingot or a casting may contain any combination of these zones mainly depending upon the casting conditions and the chemical composition of the alloy.

The development of the various zones in an ingot or a casting is seldom due to one specific mechanism only but must often be looked upon as a result of combinations between several different mechanisms during the course of solidification.

For example, the mechanisms of formation of the outer chill zone and the central equiaxed zone have been the subject of considerable interest.

The accepted explanation for formation of the outer chill zone as expressed by Chalmers (18) is that supercooling occurs in the melt in the region near the

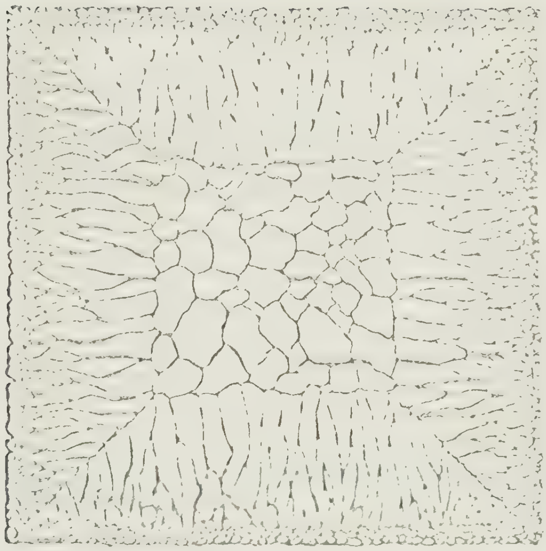


Figure 12 Sketch of ingot structure showing a chill zone, a columnar zone and an equiaxed zone. After (32).

mould wall during and immediately after pouring due to the high temperature difference between the melt and the mould wall. This creates a situation of forming numerous of small crystals in this region. Bower and Flemings (32) have, however, shown that convection in the melt causing crystal fragmentation to occur is an essential additional factor in formation of this outer chill zone.

Furthermore, the generally accepted mechanism for formation of the inner equiaxed region is that constitutional supercooling is developed in the melt immediately in front of the growing solid phase. However, an additional mechanism has been proposed by Jackson et al (33). Crystal multiplication, caused by thermal or mechanical separation of dendrite arms, plays an important role in the development of the equiaxed region.

The purpose of this second part of this work is to give a brief survey of the most important mechanisms operating in the development of the macrostructure.

2 Different mechanisms for the development of the macrostructure

Grain refinement in an ingot or a casting can be obtained by increasing the number of sites from which new crystals can grow but also by restricting growth of crystals into the melt. This can be achieved by one or more of the following mechanisms or by combinations of them.

The following division of the subject is proposed:

Nucleation
- homogeneous
- heterogeneous

Crystal multiplication
- dendrite remelting or fragmenting
- showering mechanism
- mechanical vibration

.2.1 Nucleation

.2.1.1 Homogeneous nucleation

As most of the commercial alloys contain a large amount of heterogenities which act as nucleating agents at initial undercoolings of only a few degrees. Homogeneous nucleation does not occur in these materials, and is, therefore not considered here.

.2.1.2 Heterogeneous nucleation

As usually, melts of commercial materials contain solid impurity particles of foreign nature, homogeneous nucleation is very seldom observed in these materials. It is therefore possible to make the assumption that the first grains in a melt have been nucleated heterogeneously at the initial undercooling in the melt.

Two investigators, Turnbull and Vonnegut (34) have proposed that the solid impurity particles increase the nucleation probability by reducing the magnitude of the surface energy barrier to nucleation.

There have been many attempts in literature to describe the mechanisms of heterogeneous nucleation. The vital point of this mechanism is however, the presence of particles in the melt, insoluble at the melting point of the base material. These different particles in the melt generally possess different potency of nucleation often due to the difference in atomic structures between the particle and the base material.

In practice, the nucleation of a melt will be determined by the particles of the highest potency and the number of new grains formed will be proportional to the number of such active nuclei.

Figure 13 shows the potency as well as the relative number of two different kinds of nucleating particles. If a melt is undercooled, the particles of type 1 will initiate the growth of new crystals and the latent heat released by this reaction

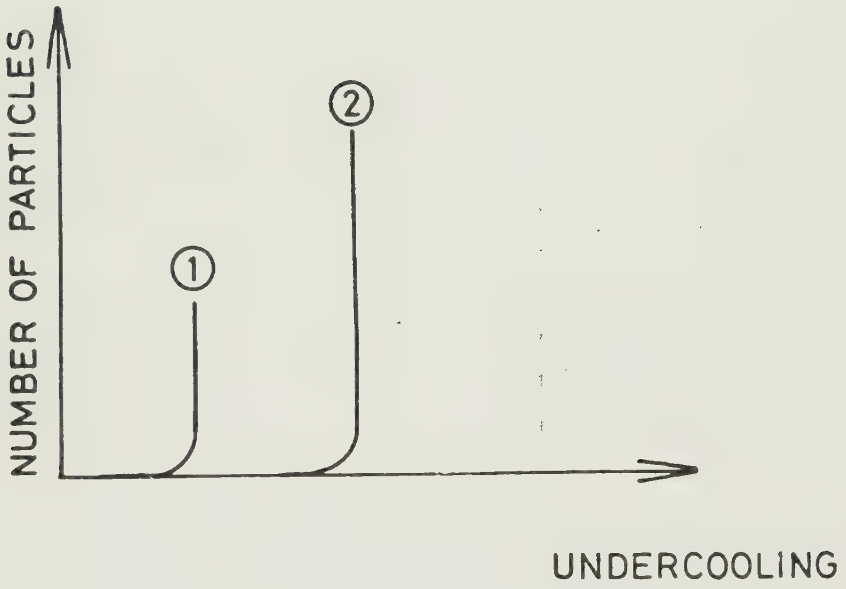


Figure 13 Number of particles as function of undercooling for two different types of heterogeneous particles.

will cause the surrounding melt to recalesce thus masking off the nucleating effect of the more numerous second type (type 2) of nuclei. Though the total number of nuclei present in the melt may be high the resulting macrostructure may, due to this mechanism, be relatively coarse.

.2.2 Crystal multiplication

.2.2.1 Dendrite remelting or fragmentation

Another way of producing grain refinement, is the dendritic remelting mechanism. One of the more recent and complete investigations on this subject was presented by Jackson et al (33) after their studies of dendritic growth in organic materials. They observed that dendrite branches fragmentates and form potential growth centers in the solution.

They conclude that fluctuations in the growth rate produce many isolated crystals by melting off dendrite arms. Such isolated crystals may be transported into the bulk liquid by thermal or mechanical convections.

This type of mechanism may also be predominant in the solidification of metal alloys, noticed in those alloys that do not contain heterogeneous nuclei of sufficient potency to activate subsequent nucleation.

Jones and Weston (35) conclude out of their observations in copper containing small amounts of oxygen, that, immediately after initial nucleation, fine, relatively pure dendrites grow rapidly into the melt and build up an enriched boundary layer at the interface by rejection of solute. Secondary branching of the dendrites must grow through this enriched layer and the necks of the branches are therefore high in solute and freeze at a lower temperature than the main stem. After this boundary layer has been penetrated, the secondary branches can grow into the purer liquid. Meanwhile the temperature of the melt will rise due to recalescence and the heat thus evolved can cause melting of the impure necks of the secondary branches causing fragmentation of the dendrite arms. These branches can be transported into the melt and there act as nuclei for further growth provided convection currents are present.

Fragmentation will occur during recalescence by this process and will produce a fine grain structure throughout the whole ingot. Althrough the remaining liquid then solidifies close to the equilibrium temperature at a slower rate - determined by the heat extraction conditions - the final grain size will depend on the extent of prior fragmentation.

Chill zone multiplication

In the undercooled melt near the mould wall, initial nucleated crystals may grow at a high rate in a branched manner. Due to the heavy convections, often present in the beginning of the freezing process, the dendrite arms easily undergo fragmentation and may act as new growth centres.

1.2.2.2 Showering mechanism

Another type of crystal multiplication, discussed by Ruddle (36) and by Southin (37), suggests that the crystals that form the equiaxed zone nucleate at the top surface of the liquid and settle under the influence of gravity to the central and lower parts of the castings there acting as nuclei.

.2.2.3 Grain refinement due to mechanical disturbance of the growth front

Finally must be mentioned another way of getting refinement namely by mechanical disturbance.

It has been proposed that the grain refining effects of vibration were produced by fragmentation of primary crystallites, thereby providing an artificial source of stable nuclei.

Grain refinement produced by vibration is virtually independent of frequency and principally controlled by the energy intensity. One theory is that vibration produces alternate pressure and rarefaction waves in the solidifying melt. These variations in pressure produce additional sites of easy nucleation.

Fredman and Wallace (38) have applicated vibration in some aluminium- and copper-base materials to study the grain refinement. They found that the materials, which have been vibrated, clearly indicate the presence of considerably finer grains.

Stirring the melt may have similar effect on the fragmentation as promoting grain refinement. Applying mechanical force in solidifying systems may also have the same effect.

4.3 Studies of the development of macrostructure in some copper-based alloys

4.3.1 Introduction

Principle grain refinement mechanisms were studied and discussed by Bäckerud and Liljenvall in (3) using more or less idealized binary copper-based systems in the experiments.

In the solidification study of commercially available copper alloys made by Liljenvall (4), it has not been possible to control the purity of the base material and the metallurgical prehistory of the samples used in that investigation was unknown. It can therefore not be expected to obtain the same simple solidification behaviour for these alloys as in the previous study.

In (3) Bäckerud and Liljenvall have presented a system for characterization of the obtained macrostructures which is presented on page 366 and figures 2 and 3 in (3). Four different types of operating mechanisms can be distinguished. In another work concerning commercial copper alloys, Liljenvall (4) has observed the development of three of these different types and that several alloys show macrostructures, which may develop as a result of a co-operation of these mechanisms.

3.2 Limited initial nucleation only

As can be expected, alloys, which can solve element such as zinc in matrix and thus produce a little value for the growth undercooling will develop such macro-structures which can be fo ind in the lower left quadrant in the figure 2 in (3).

These types of alloys are subjected to an initial nucleation process and show a completely columnar structure.

Colton and Margolis (39) have observed in their solidification studies of a copper-5 % zinc alloy, that the solidified columnar structure, which consists of a α-solid solution of zinc in copper, would behave much like pu e copper, cooled under the same conditions.

The same observations is made by Bäckerud and Liljenvall (3) who studied the development of the solidification structure at increasing concentration under unchanged cooling conditions, 25 degC/min. The columnar structure persists through the concentration interval investigated (0. 01 - 5. 0 % zinc) as seen from the macrostructures; figure 18 in (3).

Typical examples of these completely columnar structures for commercial copper-based alloys are, for example, the cartridge brass (70Cu/30Zn), aluminium brass and copper-iron alloy, with a hypo-peritectic iron concentration.

.3.3 Limited initial and frequently subsequent nucleation

In commercial alloys, which contain elements with low solubility in the matrix, as expected, an outer crown of initial nucleated crystals, which have developed at the initial part of the solidification process, surrounds the fine-grained inner equiaxed structure, obtained by a secondary nucleation mechanism. From this it can be concluded that the critical nucleation temperature for the heterogeneous particles in the melt lies above that for the growth undercooling.

As shown by Bäckerud and Liljenvall (3), the influence of lead concerning the transition between columnar and equiaxed crystals occurs already at a very low concentration or 0. 1 % lead in pure copper, when studied at a cooling rate of 25 degC/min. As seen from the macrophotos in (3) from the copper-lead system, at 0. 1 % lead, there is a little but still an outer zone of columnar structure which surrounds the equiaxed zone in the middle of the ingot.

As a result of low solubility in the copper-matrix, lead is enriched in front of the growing crystals and a pronounced growth undercooling is thereby developed. However, at a special value on this growth undercooling, heterogeneous particles in the melt are activated and give rise to a subsequent nucleation process producing equiaxed crystals in the middle of the ingot.

This grain refinement action has been observed by Colton and Margolis (39) in their solidification studies of copper-lead alloys. An addition of 5 % lead to copper produces a markedly grain refinement of the macrostructure, which is in agreement with the above mentioned observations.

Gould et al (40) have found that a pronounced refinement in the solidified structure was obtained at a concentration of 2.42 % iron in copper.

The same appearance in the development of the macrostructure has been noticed by Bäckerud and Liljenvall (3) in an earlier work concerning solidification studies of copper-base alloys. Thus the system copper-cobalt shows a peritectic reaction and this effect on the macrostructure has been reported, see figure 21 in (3).

The influence on the peritectic reaction on the grain refinement has been observed i.e. by Iwasé et al (41), who made experiments to find out the association between the two different structures developed at hypo- and hyper-peritectic iron compositions in copper. They made investigations on several systems of which the copper-iron and the copper-aluminium-iron systems are of interest and are mentioned here.

They observed that the alloys with a composition less than that necessary for the peritectic reaction, crystallize in the α-form and consist of large grains. The specimens with the hyper-peritectic concentration undergo the peritectic reaction and the resulting macrostructures consist of very fine grains.

They showed that the grain refinement is closely related to the peritectic reaction, which is characteristic for these two systems. The curves in figures 14 a and b show the grain size as function of the iron composition in the two mentioned copper-base systems.

This grain refinement effect has also been observed in other alloy systems. The effect was mentioned already by Iwasé et al (41) who made further investigations in the systems: Cu-Co, Cu-Fe-Zn, Cu-Fe-Sn, Cu-Fe-Mn, Cu-Fe-Ni, Cu-Co-Sn, and Cu-Co-Ni. The grain refinements, observed in these systems, are very much alike those found in the Cu-Fe-system, and closely related to the peritectic reaction within the system.

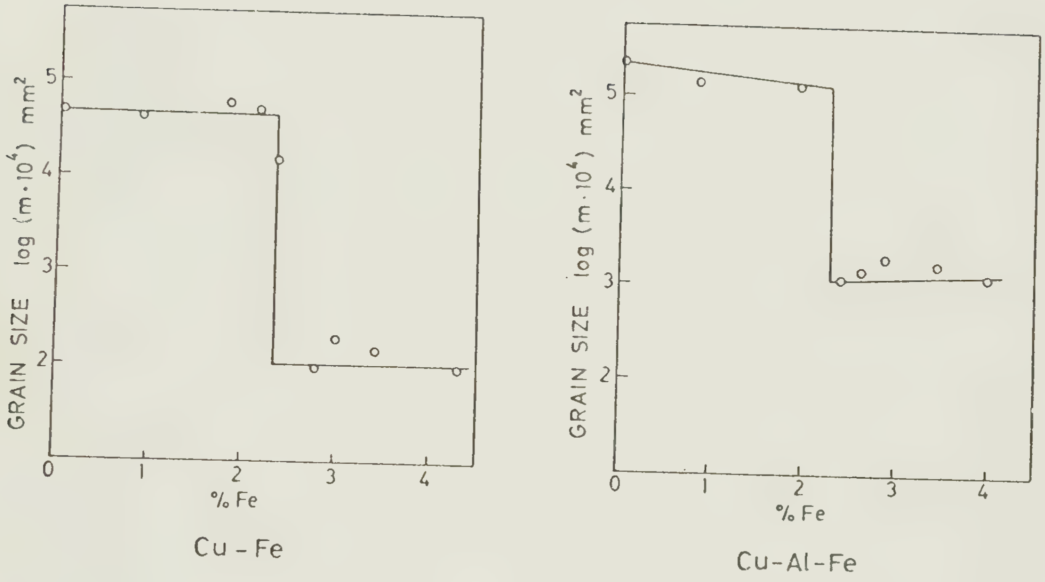


Figure 14 The grain size at various iron-concentrations in two a and b different copper-rich alloys. After (41).

4.3.1.4 The peritectic reaction

As a summary, it can be pointed out that the importance of the peritectic reaction as a grain refinement mechanism is demonstrated by the fact that additions of less amount of alloying additions than that required to undergo the reaction did not produce grain refinement if suitable inoculants are absent in the melt.

When a copper-iron alloy of hyper-peritectic composition is cooled to a temperature slight below the liquidus line, the iron-rich γ-phase will be separated from the melt. This phase reacts with the liquid at the peritectic temperature and forms the α-phase. The maintenance of this reaction requires solute atoms from the γ-phase to diffuse through the new-formed α-layer when solvent atoms from the liquid must migrate to the more and more enveloped γ-phase. Consequently, this reaction proceeds rather slowly, thus effectively reducing the growth of crystals in the melt. Moreover, the α-phase surrounding the γ-phase particles presents ideal sites for nucleation from the lower temperature α-phase, whether the peritectic reaction goes to completion or not. Typical examples, obtained in this case are thus the copper-iron alloy with a hyper-peritectic iron concentration. The copper-5 % cobalt alloy, mentioned above, figure 21 in (3), also shows a fine equiaxed structure due to the peritectic reaction.

5. SUMMARY

The first part of this thesis deals with the development of microstructure, obtained at different thermal conditions in the melt. The thermal gradient can be obviously negative, obviously positive or near zero and the different structures obtained in the special cases are discussed.

This part of the work concludes with the development of the microstructure in some copper-based alloys.

The second part of this thesis deals with different mechanisms in the development of macrostructure. The nucleation and crystal multiplication processes are outlined and finally the obtained macrostructure of some copper-based alloys are discussed.

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